

# Tar and/or oil pitch with a low content of polycyclic aromatic substances and a method for the preparation thereof

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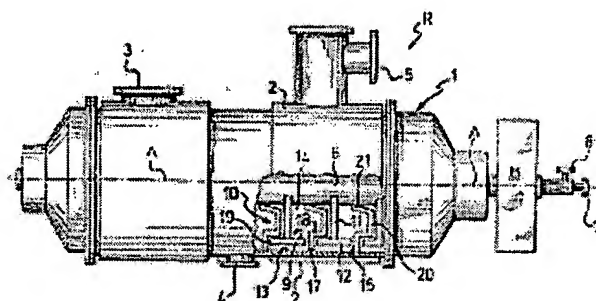
## Cited documents:

EP0510315
US5746906
US5121992
XP002081348
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## Abstract of EP0957150

A tar and/or oil pitch has a low content of polycyclic aromatic substances and is characterized in that it has a benzo $\alpha$ pyrene content less than or equal to 5 ppm, and in that it has optical anisotropy of less than 1%; it is prepared by means of a method in which a residue with a low softening point from the primary distillation of tar and/or petroleum or a mixture of the residue with tar and/or petroleum is distilled with continuous mixing in an evaporator having a heat-exchange area:volume ratio of between  $1 \text{ m}^2/\text{m}^3$  and  $200 \text{ m}^2/\text{m}^3$ , at a pressure less than or equal to 10 mbars, and at a temperature of between 250 DEG C and 360 DEG C, for a period of at least 20 minutes; the pitch according to the invention is particularly suitable for use as a binding agent in the production of electrodes, refractory materials or special graphitized materials, as an impregnating agent, and as a raw material for the production of paints, pitch coke and rechargeable batteries.



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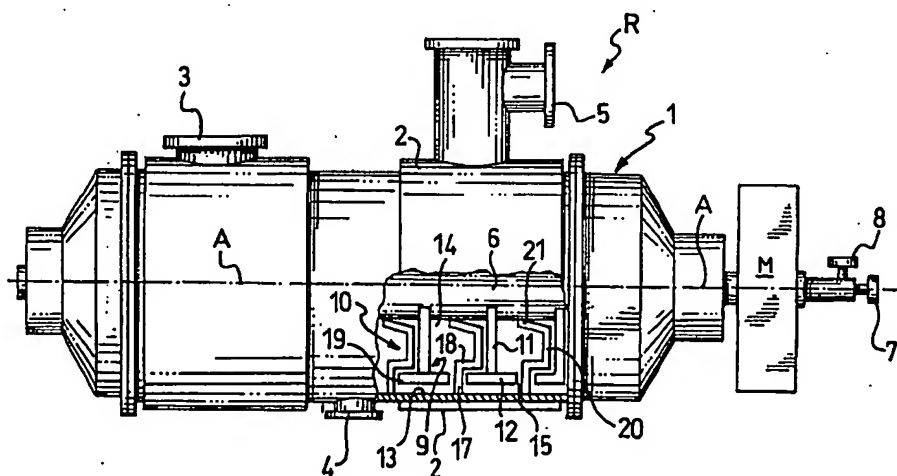
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(54) **Tar and/or oil pitch with a low content of polycyclic aromatic substances and a method for the preparation thereof**

(57) A tar and/or oil pitch has a low content of polycyclic aromatic substances and is characterized in that it has a benzo[a]pyrene content less than or equal to 5 ppm, and in that it has optical anisotropy of less than 1%; it is prepared by means of a method in which a residue with a low softening point from the primary distillation of tar and/or petroleum or a mixture of the residue with tar and/or petroleum is distilled with continuous mixing in an evaporator having a heat-exchange area:volume ratio of between 1 m<sup>2</sup>/m<sup>3</sup> and 200 m<sup>2</sup>/m<sup>3</sup>,

at a pressure less than or equal to 10 mbars, and at a temperature of between 250°C and 360°C, for a period of at least 20 minutes; the pitch according to the invention is particularly suitable for use as a binding agent in the production of electrodes, refractory materials or special graphitized materials, as an impregnating agent, and as a raw material for the production of paints, pitch coke and rechargeable batteries.



## Description

[0001] The present invention relates in general to a tar or oil pitch with a low content of polycyclic aromatic substances.

5 [0002] In particular, the present invention relates to a pitch of the aforementioned type which is substantially free of benzo[a]pyrene.

[0003] The terms "tar pitch" and "oil pitch" are intended to define residues which can be produced, respectively, by the distillation of coal tar and of petroleum fractions and/or residues thereof resulting from processes such as thermal or catalytic cracking.

10 [0004] The present invention also relates to a method of producing tar and/or oil pitches which are substantially free of benzo[a] pyrene.

[0005] It is known that an isotropic pitch based on aromatic compounds and having a low softening point, normally below 150°C, can be produced by the primary distillation of tar or of petroleum.

15 [0006] It is also possible to remove a certain quantity of oils from pitch with a low softening point (soft pitch) by subsequent distillation, generally under vacuum and possibly in the presence of a stripping agent, and thus to produce a residue with a higher softening point (hard pitch).

[0007] The aforementioned pitches are widely used in various industrial applications but they have the serious disadvantage of containing various aromatic compounds which are suspected of having or which have carcinogenic properties, and the presence of which leads to considerable problems due to environmental impact and constitutes a potential hazard to workers' health.

[0008] Of these aromatic compounds, the one which has been investigated most is benzo[a]pyrene; this compound, which has been confirmed to be carcinogenic, is found in concentrations of about 0.5-1.5% by weight in soft pitches derived from tar and about 0.1-1% by weight in soft pitches derived from petroleum.

25 [0009] In hard pitches, on the other hand, the concentration of benzo[a]pyrene is reduced as a result of the second distillation and is generally within the range of 4,000-12,000 ppm.

[0010] The presence of benzo[a]pyrene in pitches is in any case not desirable and, moreover, the current regulations classify pitches having a benzo[a]pyrene content greater than 50 ppm as carcinogenic products and provide for particular care and attention during their handling.

30 [0011] For this reason, special methods of distilling residues from the primary distillation of tar or of petroleum have been devised and sometimes adopted in order to reduce as far as possible the benzo[a]pyrene content in the final pitches.

[0012] European patent EP 0 510 315 describes a method of producing pitches having a benzo[a]pyrene content of less than 50 ppm in which a residue of the primary distillation of tar is distilled at a temperature of 300-380°C and at a pressure of less than 1 mbar in an evaporator having a heat-exchange area:volume ratio of between 330 and 10,000 m<sup>2</sup>/m<sup>3</sup>, with the residue spending a period of 2-10 minutes in the evaporator.

35 [0013] In Examples 1, 2 and 3 of this patent, it is reported that, by distilling the aforementioned residue in a thin-layer evaporator operating at a temperature of 300°C, 320°C, and 340°C and at a pressure of 1 mbar, with an average period of about 5 minutes spent in the evaporator, pitches containing 35 ppm, 20 ppm and 20 ppm of benzo[a]pyrene, respectively, were produced.

40 [0014] However, it is clear from a comparison of Examples 2 and 3 of EP 0 510 315 that even a considerable increase in the distillation temperature (20°C) does not permit a further reduction of the benzo[a]pyrene content in the final pitches which, in fact, is never less than 20 ppm in the examples given in the above-mentioned document.

[0015] In EP 0 510 315, the German patent DE 3702720, which relates to a method of preparing a tar pitch with a high softening point and a low content of substances insoluble in quinoline, is cited as prior art.

45 [0016] In this method, a filtered tar pitch having a low softening point is distilled in a thin-layer evaporator at a temperature of 300-425°C and at a pressure no greater than 10 mbars.

[0017] In DE 3702720 it is taught that, in order to have a low content of substances insoluble in quinoline in the final pitches, the average time spent by the filtered pitch in the evaporator should be very short and in fact, in Examples 1 and 2, with distillation carried out at a pressure of 1 mbar and at a temperature within the range of 300-380°C, it is always less than 1 minute.

50 [0018] However, in EP 0 510 315, Example 2 of the aforementioned German application is cited, and it is stated that the pitch obtained in accordance with this example still contains 140 ppm of benzo[a]pyrene and the method described in DE 3702720 is therefore not suitable for producing a pitch with a low benzo[a]pyrene content in the sense indicated by the current regulations.

55 [0019] In fact, it is clear from the above-mentioned examples of EP 0 510 315 and DE 3702720 that, in order to eliminate the benzo[a]pyrene from the primary residues, it is important to extend the time spent by these residues in the evaporator rather than to increase the distillation temperature.

[0020] However, it is well known that the subjection of residues of the primary distillation of tar or oil to temperature

conditions of 350-450°C for a prolonged period results in the progressive formation therein of an optically anisotropic ordered structure which is known as a mesophase and is quantifiable by suitable microscopic techniques in polarized light, and the presence of which is undesirable for some industrial uses of the final pitches as binding and impregnation agents.

5 [0021] For this reason, in the prior art, the subsequent distillation of residues resulting from the primary distillation of tar or petroleum is performed in evaporators which have a large heat-exchange area, such as thin-layer or thin-film evaporators which allow the residues to have short contact times with the exchange surface, generally less than 10 minutes, so as to reduce the mesophase content of the final pitches as far as possible.

10 [0022] Both in the method of EP 0 510 315 and in that of DE 3702720, pitches having optical anisotropy of less than 2% are thus produced by distillation in thin-layer evaporators.

[0023] However, thin-layer or thin-film evaporators have the disadvantage that it is extremely difficult to achieve a uniform layer of pitch on their exchange surfaces so that exchange efficiency is not particularly high.

15 [0024] The technical problem upon which the present invention is based is that of providing tar and/or oil pitches which are substantially free of benzo[a]pyrene and which, at the same time, also have low optical anisotropy so that they can be used in all industrial applications which require substantially isotropic pitches.

[0025] This problem is solved by a tar and/or oil pitch, characterized in that it has a benzo[a]pyrene content less than or equal to 5 ppm and optical anisotropy of less than 1%.

[0026] As well as having optical anisotropy of less than 1%, the pitches of the invention are preferably characterized in that they are free of benzo[a]pyrene.

20 [0027] According to one embodiment, the pitches of the invention are further characterized in that they have a content of less than 50 ppm, preferably less than 5 ppm, of each of the following polycyclic aromatic compounds: benzo[a]anthracene, chrysene, benzo[a]fluoranthene, benzo[k]fluoranthene, benzo[b]fluoranthene, benzo[e]pyrene, indeno[1,2,3-c,d]pyrene, dibenzo[a,h]anthracene and benzo[g,h,i]perylene.

25 [0028] According to another embodiment, the pitches of the invention are further characterized in that they are free of the above-mentioned polycyclic aromatic compounds.

[0029] The present invention also relates to a method of preparing tar and/or oil pitches substantially free of benzo[a]pyrene, the method comprising the steps of:

- performing a first distillation of tar and/or petroleum so as to produce a residue with a low softening point;
- 30 - supplying the residue or a mixture of the residue with tar and/or petroleum into an evaporator having a heat-exchange area:volume ratio of between 1 m<sup>2</sup>/m<sup>3</sup> and 200 m<sup>2</sup>/m<sup>3</sup>, the residue or mixture being kept in a state of continuous mixing;
- distilling the residue or the mixture with continuous mixing, in the evaporator, at a pressure less than or equal to 10 mbars and at a temperature of between 250°C and 360°C, for a period of at least 20 minutes;
- 35 - discharging the pitch from the evaporator and, at the same time, recovering a distillate.

[0030] Preferably, the period for which the residue or the mixture is distilled in the evaporator is between 20 minutes and 10 hours.

40 [0031] Surprisingly, it has been found that, as well as being free of benzo[a]pyrene or having a content of this compound less than or equal to 5 ppm, the pitch produced in the manner described above also has optical anisotropy of less than 1%.

45 [0032] Thus, in contrast with the teachings of the prior art, in the method of the invention, the removal of the benzo[a]pyrene from the above-mentioned residue or from the above-mentioned mixture by distillation for long periods is not accompanied by the formation of unacceptable quantities of mesophase in the final pitch. Naturally, the operative temperature and vacuum conditions of the evaporator and the distillation time can be selected within the above-mentioned ranges according to the chemico-physical characteristics and the benzo[a]pyrene content of the residue or of the mixture to be distilled so as to produce a final pitch substantially free of this compound.

50 [0033] It has also been found that the pitches produced by the method of the invention can be produced free of the following polycyclic aromatic compounds: benzo[a]anthracene, chrysene, benzo[a]fluoranthene, benzo[k]fluoranthene, benzo[b]fluoranthene, benzo[e]pyrene, indeno[1,2,3-c,d]pyrene, dibenzo[a,h]anthracene and benzo[g,h,i]perylene, or, alternatively, have a content of less than 50 ppm, preferably less than 5 ppm, of the above-mentioned compounds.

55 [0034] This renders the method of the invention particularly advantageous, since some of the above-mentioned polycyclic aromatic compounds, that is: benzo[a]anthracene, benzo[a]fluoranthene, benzo[k]fluoranthene, benzo[b]fluoranthene and dibenzo[a,h]anthracene, are possibly or probably carcinogenic to man, whilst the other compounds mentioned above are suspected of having this property.

[0035] In the method of the invention, the apparatus used for the distillation of the residue from the primary distillation of tar and/or petroleum or of the mixture of this residue with tar and/or petroleum is of particular importance and should have a heat-exchange area:volume ratio of between 1 m<sup>2</sup>/m<sup>3</sup> and 200 m<sup>2</sup>/m<sup>3</sup>, preferably between 5 m<sup>2</sup>/m<sup>3</sup> and 60

$\text{m}^2/\text{m}^3$ , and should enable the residue or the mixture to be mixed continuously during distillation.

[0036] According to a preferred embodiment of the method of the invention, the distillation of the above-mentioned residue or of the above-mentioned mixture is performed in an evaporator which at the same time acts as a mixer and which comprises a cylindrical body provided with a jacket for heating its internal wall, at least one inlet opening for the residue or the mixture, at least one outlet opening for the final pitch, at least one distillate-recovery opening connected to a system for applying a reduced pressure to the interior of the cylindrical body, and a rotary shaft which can be heated and is supported for rotating in the cylindrical body, and along the axis of which radial mixing elements, which may also be capable of being heated, are disposed.

[0037] According to one embodiment of the method of the invention, the evaporator further comprises opposed mixing elements fixed radially to the internal wall of the cylindrical body and interposed between the radial elements in order to facilitate the removal of the residue or of the mixture from the peripheral surface of the shaft and from the surfaces of the mixing elements.

[0038] Preferably, the radial mixing elements comprise disc sectors to which mixing bars are fixed and the opposed mixing elements are substantially hook-shaped with at least one portion skimming the disc sectors and at least one portion skimming the peripheral surface of the shaft.

[0039] The rotary shaft of the evaporator is heated by means of a diathermic fluid which flows through an internal circuit thereof and the mixing elements (the disc sectors and the bars) may also be heated by the same fluid; in this case, ducts through which the fluid can flow and which are in communication with the heating circuit of the rotary shaft are formed in the mixing element.

[0040] With the use of an evaporator of this type, the distillation of the residue of the primary distillation of tar and/or petroleum or of the mixture of the residue with tar and/or petroleum according to the method of the invention comprises the steps of:

- supplying the residue or the mixture into the evaporator in which the internal wall, the rotary shaft, and possibly the mixing elements, are kept at a temperature of 250-360°C, the rotary shaft is rotated at a speed of 1-150 revolutions/minute, and the pressure is equal to or less than 10 mbars, the mixer having a heat-exchange area:volume ratio between 1  $\text{m}^2/\text{m}^3$  and 200  $\text{m}^2/\text{m}^3$ ;
- mixing the residue or the mixture for a period of at least 20 minutes by means of the mixing elements in a relationship permitting thermal exchange with the internal wall of the evaporator, the rotary shaft and, possibly, the mixing elements;
- discharging from the evaporator a pitch substantially free of benzo[a]pyrene and having optical anisotropy of less than 1% and, at the same time, recovering a distillate.

[0041] During the mixing step of the method of the invention, if the evaporator comprises the above-mentioned opposed fixed mixing elements, these facilitate the removal of the residue or of the mixture from the peripheral surface of the rotary shaft and from the surfaces of the mixing elements.

[0042] The above-described evaporator-mixers, which may be used continuously, semi-continuously or for batch operation, have the advantage of highly efficient heat exchange and mass transfer since the product treated therein is mixed continuously in conditions permitting thermal exchange with contact surfaces all of which can be heated and which at the same time are cleaned of the product by any opposed mixing elements.

[0043] These evaporators are known *per se* and are used for performing various processes such as drying, evaporation, sublimation, etc., by the thermal and mechanical treatment of products in liquid, paste or powder form.

[0044] However, they are particularly advantageous in the treatment of residues of the primary distillation of tar and/or petroleum in order to produce pitches substantially free of benzo[a]pyrene and with low optical anisotropy.

[0045] The pitches produced by the method of the invention can be used in various industrial applications for which an isotropic pitch is required.

[0046] They can be used, for example, as binding agents in the production of electrodes, refractory materials or special graphitized materials, as impregnating agents, or as a raw material for the production of paints, pitch coke and rechargeable batteries.

[0047] In these applications, at least one viscosity-modifying agent is generally added to the pitches of the invention before use.

[0048] In fact, with the method of the invention, in addition to the substantial removal of benzo[a]pyrene and a large number of polycyclic aromatic compounds from the residues subjected to distillation, most of the volatile oily component of these residues is also removed, so that the pitches of the invention are produced with a viscosity too high for them to be usable directly in most cases.

[0049] For some applications, however, the pitch thus produced is advantageously used directly without the aid of viscosity-modifying agents.

[0050] Viscosity-modifying agents which may be used are, for example, aromatic oils, resins, bituminous products

miscible with pitches, etc., selected in dependence on the final use of the pitches.

[0051] In any case, the at least one viscosity-modifying agent added to the pitches of the invention is advantageously substantially free of benzo[a]pyrene so that compositions comprising the pitches of the invention and at least one such agent can be used in the various applications without problems of environmental impact or risk to workers' health.

5 [0052] The characteristics and advantages of the present invention will become clear from the following description of some examples of the implementation of the method of the invention, given with reference to the drawing appended by way of non-limiting example.

[0053] The drawing is a schematic side view of an evaporator, partially open, which is usable for implementing the method of the invention, and is of the type described, for example, in US patent 5,121,992, the text of which should be referred to for a detailed description.

10 [0054] With reference to the drawing, an evaporator, generally indicated R, comprises a cylindrical body 1 arranged with its longitudinal axis horizontal, surrounded by a heating jacket 2 through which a diathermic fluid is intended to flow, and having an inlet opening 3 for a residue or a mixture to be distilled, an outlet opening 4 for the final pitch, and a distillate-recovery opening 5 connected to a system (not shown) for applying a reduced pressure to the interior of the cylindrical body 1.

15 [0055] A shaft 6 supported for rotating in the cylindrical body 1 about a rotation axis A is heated by a diathermic fluid which is admitted to its interior through an opening 7 and emerges therefrom through an opening 8. A motor M is provided for driving the shaft 6 at a speed of between 1 and 150 revolutions/minute.

[0056] Arranged along the longitudinal axis of the shaft 6 are radial mixing elements 9 between which opposed mixing elements 10, arranged radially on the internal wall 13 of the cylindrical body 1, are interposed.

20 [0057] The mixing elements 9 comprise disc sectors 11 to which mixing bars 12 are fixed. The disc sectors 11 rotate together with the shaft 6 and the bars 12 pass a small distance from the internal wall 13 of the cylindrical body 1.

[0058] The internal wall 13 is thus cleaned of the product subjected to distillation in the evaporator R.

25 [0059] Between adjacent disc sectors 11 there is an empty space 14 for the mixing of the product to be treated and between adjacent bars 12 there is an empty space 15 through which a support 17 of an opposed mixing element 10 fixed to the internal wall 13 of the cylindrical body 1 can pass.

[0060] The opposed mixing elements 10 are substantially hook-shaped and each comprises a support 17 and portions 18, 20 and 21.

30 [0061] The support 17 is arranged radially relative to the shaft 6 and is joined to the portion 18 which is parallel to the axis of rotation A.

[0062] The portion 18 forms, together with the respective portion of the mixing bar 12, a slot 19 through which the bar 12 can move.

[0063] The product to be treated is thus also forced between the portion 18 and the internal wall 13 of the cylindrical body 1 and is mixed continuously.

35 [0064] The portion 18 in turn is joined, in the region of the disc sector 11, to a radial portion 20 which extends as far as the vicinity of the shaft 6.

[0065] The purpose of this portion 20 is to remove the product from the disc sectors 11, preventing the formation of deposits on these sectors and, at the same time, to mix the product between the portion 20 and the disc sectors 11, thus improving the mixing action.

40 [0066] The portion 20 in turn is joined to a portion 21 parallel to the peripheral surface of the shaft 6 and inclined away from the section 20 in the direction of rotation of the shaft 6.

[0067] The purpose of this portion 21 is to remove the product from the peripheral surface of the shaft 6.

[0068] The drawing shows opposed mixing elements 10 which skim the surface of the disc sectors 11 on one side.

45 [0069] Similar opposed mixing elements (not shown) may be provided in the cylindrical body 1 in an opposite arrangement so as to remove the product from the other surface of the disc sectors 11 with a corresponding radial portion, and from the peripheral surface of the shaft 6 which is not cleaned by the portion 21.

[0070] According to the method of the invention, a residue from the primary distillation of tar and/or petroleum or a mixture of this residue with tar and/or petroleum is supplied to the mixer R through the inlet opening 3 and is taken from this inlet and worked mechanically by the mixing elements 9 of the shaft 6 which are kept rotating at a suitable speed.

50 [0071] The residue or mixture is then mixed continuously by the mixing elements 9 in a relationship permitting thermal exchange with the internal wall 13 of the cylindrical body 1 and with the shaft 6 which are kept at a predetermined temperature and in conditions of reduced pressure in the cylindrical body 1, applied through the opening 5 thereof, through which the distillate is also recovered.

55 [0072] The mixing of the residue or of the mixture takes place substantially in the space 14, in the slot 19 and between the radial portion 20 and the disc sectors 11 and, at the same time, it is removed from the surfaces of the disc sectors 11 by means of the radial portions 20 and from the peripheral surface of the shaft 6 by means of the portions 21 of the opposed mixing elements 10.

[0073] After a suitable distillation time, a pitch substantially free of benzo[a]pyrene is then discharged from the outlet

opening 4.

[0074] Naturally, for technical and contingent reasons, many modifications may be applied to the above-described evaporator for example, to its shape, its size and the arrangement of its component parts, or it may have one or more inlet and outlet openings and one or more heating and cooling jackets, for example, in order to achieve a temperature gradient and thus to implement an exchange of heat for the purposes of particular working requirements.

[0075] Moreover, the method of the invention may also be implemented with the use of other evaporators based on the same operating principle as the evaporator described above, for example, evaporators of the type described in US patent 5,407,266 comprising two or more rotary shafts which carry radial mixing elements mating with one another in a manner such that the surfaces of the mixing elements of one shaft are continuously cleaned by the mixing elements of another shaft and *vice versa* during the processing of the product.

#### EXAMPLE 1

[0076] 5.4 kg of a residue produced by the primary distillation of coal tar and having the characteristics given in Table 1A was supplied to an evaporator exactly the same, in its basic elements, as the apparatus described above, produced by the firm LIST AG and sold under the name DT-B.

TABLE 1A

Parameters	Analytical method	Value
Mettler softening temperature (°C)	ASTM D 3104	107.5
Insoluble in quinoline Q.I. (% by weight)	ISO 6791	12.4
Insoluble in toluene T.I. (% by weight)	ISO 6376	36.1
Alcan coke yield (% by weight)	ASTM D 4715	59.3
Benzo[a]anthracene (ppm)	GLC	9060
Benzo[e]pyrene (ppm)	GLC	9170
Benzo[a]pyrene (ppm)	GLC	10920
Indeno[1,2,3-c,d]pyrene (ppm)	GLC	11510
Dibenzo[a,h]anthracene(ppm)	GLC	10300
Benzo[g,h,i]perylene (ppm)	GLC	5080
Chrysene (ppm)	GLC	9750
Benzo[a]fluoranthene + Benzo[k]fluoranthene (ppm)	GLC	13850
Benzo[b]fluoranthene (ppm)	GLC	6210
Optical anisotropy (% by volume)	ASTM D 4616	0

[0077] This evaporator had a heat-exchange area:volume ratio of about 50 m<sup>2</sup>/m<sup>3</sup>.

[0078] The internal wall of the evaporator was heated to a temperature of about 320°C, the pressure inside the evaporator was brought to about 0.4 mbars, and the rotary shaft was rotated at a constant speed of 60 revolutions/minute.

[0079] After a period of about 45 minutes spent by the residue in the evaporator in the conditions given above, 3.1 kg of a tar pitch was discharged and the distillate was recovered separately and condensed.

[0080] A series of analytical determinations was performed on the pitch thus obtained, the results of which are given in Table 1B:

TABLE 1B

Parameters	Analytical method	Value
Insoluble in quinoline Q.I. (% by weight)	ISO 6791	24.3
Insoluble in toluene, T.I. (% by weight)	ISO 6376	67.2
Alcan coke yield (% by weight)	ASTM D 4715	89.6

TABLE 1B (continued)

Parameters	Analytical method	Value
Benzo[a]anthracene (ppm)	GLC and HPLC	0
Benzo[e]pyrene (ppm)	GLC and HPLC	0
Benzo[a]pyrene (ppm)	GLC and HPLC	0
Indeno[1,2,3-c,d]pyrene (ppm)	GLC and HPLC	0
Dibenzo[a,h]anthracene (ppm)	GLC and HPLC	0
Benzo[g,h,i]perylene (ppm)	GLC and HPLC	0
Chrysene (ppm)	GLC and HPLC	0
Benzo[a]fluoranthene + Benzo[k]fluoranthene (ppm)	GLC and HPLC	0
Benzo[b]fluoranthene (ppm)	GLC and HPLC	0
Optical anisotropy (% by volume)	ASTM D 4616	0

[0081] The above-mentioned pitch showed no trace of benzo[a]pyrene or of the other polycyclic aromatic compounds given in Tables 1A and 1B, determined by gas-liquid chromatography (GLC) and liquid-liquid chromatography (HPLC) and also had zero optical anisotropy.

## EXAMPLE 2

[0082] 6 kg of a residue produced by the primary distillation of residues of the cracking of petroliferous fractions and having the characteristics given in Table 2A were supplied to the evaporator of Example 1.

TABLE 2A

Parameters	Analytical method	Value
Mettler softening temperature (°C)	ASTM D 3104	109.0
Insoluble in quinoline Q.I. (% by weight)	ISO 6791	0.8
Insoluble in toluene, T.I. (% by weight)	ISO 6376	9.1
Alcan coke yield (% by weight)	ASTM D 4715	48.3
Benzo[a]anthracene (ppm)	GLC	3770
Benzo[a]pyrene (ppm)	GLC	2920
Benzo[a]pyrene (ppm)	GLC	3240
Indeno[1,2,3-c,d]pyrene (ppm)	GLC	1040
Dibenzo[a,h]anthracene (ppm)	GLC	1150
Benzo[g,h,i]perylene (ppm)	GLC	650
Chrysene (ppm)	GLC	4940
Benzo[a]fluoranthene + Benzo[k]fluoranthene (ppm)	GLC	2230
Benzo[b]fluoranthene (ppm)	GLC	2180
Optical anisotropy (% by volume)	ASTM D 4616	0

[0083] The internal wall of the evaporator was heated to a temperature of about 320°C, the pressure inside the evaporator was brought to about 0.4 mbars, and the rotary shaft was rotated at a constant speed of 30 revolutions/minute.

[0084] After a period of about 30 minutes spent by the residue in the evaporator in the conditions given above, 3.5 kg of an oil pitch was discharged and the distillate was recovered separately and condensed.

[0085] A series of analytical determinations was performed on the pitch thus produced, the results of which are given in Table 2B:



TABLE 2B

Parameters	Analytical method	Value
Insoluble in quinoline Q.I. (% by weight)	ISO 6791	1.1
Insoluble in toluene T.I. (% by weight)	ISO 6376	17.4
Alcan coke yield (% by weight)	ASTM D 4715	71.8
Benzo[a]anthracene (ppm)	GLC and HPLC	0
Benzo[e]pyrene (ppm)	GLC and HPLC	0
Benzo[a]pyrene (ppm)	GLC and HPLC	0
Indeno[1,2,3-c,d]pyrene (ppm)	GLC and HPLC	0
Dibenzo[a,h]anthracene (ppm)	GLC and HPLC	0
Benzo[g,h,i]perylene (ppm)	GLC and HPLC	0
Chrysene (ppm)	GLC and HPLC	0
Benzo[a]fluoranthene + Benzo[k]fluoranthene (ppm)	GLC and HPLC	0
Benzo[b]fluoranthene (ppm)	GLC and HPLC	0
Optical anisotropy (% by volume)	ASTM D 4616	0

[0086] The above-mentioned pitch showed no trace of benzo[a]pyrene or of the other polycyclic aromatic compounds given in Tables 2A and 2B, determined by gas-liquid chromatography (GLC) and liquid-liquid chromatography (HPLC), and also had zero optical anisotropy.

#### EXAMPLE 3

[0087] 5.6 kg of a mixture constituted by 80 parts by weight of the residue of Example 1 having the characteristics given in Table 1A and 20 parts by weight of the residue of Example 2 having the characteristics given in table 2B was supplied to the evaporator of Example 1.

[0088] The internal wall of the evaporator was heated to a temperature of about 320°C, the pressure inside the evaporator was brought to about 0.4 mbars, and the rotary shaft was rotated at a constant speed of 60 revolutions/minute.

[0089] After a period of about 30 minutes spent by the residue in the evaporator in the conditions given above, 3.3 kg of a pitch was discharged and the distillate was recovered separately and condensed.

[0090] The pitch showed no trace of benzo[a]pyrene or of the other polycyclic aromatic compounds given in the tables of the previous examples, determined by gas-liquid chromatography (GLC) and liquid-liquid chromatography (HPLC), and also had zero optical anisotropy.

#### EXAMPLE 4

[0091] 5.5 kg of a residue produced by the primary distillation of coal tar and having the characteristics given in Table 1A was supplied into an evaporator with two rotary shafts both having mixing elements coupled with one another, produced by the firm LIST AG and sold with the name CRP.

[0092] This evaporator had a heat-exchange area:volume ratio of about 50 m<sup>2</sup>/m<sup>3</sup>.

[0093] The internal wall of the evaporator was heated to a temperature of about 320°C, the pressure inside the evaporator was brought to about 0.4 mbars, and the rotary shaft was rotated at a constant speed of 60 revolutions/minute.

[0094] After a period of about 90 minutes spent by the residue in the evaporator in the conditions given above, 3.2 kg of a tar pitch was discharged and the distillate was recovered separately and condensed.

[0095] A series of analytical determinations was performed on the pitch thus produced, the results of which are given in Table 4B:

TABLE 4B

Parameters	Analytical method	Value
Insoluble in quinoline Q.I. (% by weight)	ISO 6791	25.3
Insoluble in toluene T.I. (% by weight)	ISO 6376	68.0
Alcan coke yield (% by weight)	ASTM D 4715	90.6
Benzo[a]anthracene (ppm)	GLC and HPLC	0
Benzo[e]pyrene (ppm)	GLC and HPLC	0
Benzo[a]pyrene (ppm)	GLC and HPLC	0
Indeno[1,2,3-c,d]pyrene (ppm)	GLC and HPLC	0
Dibenzo[a,h]anthracene (ppm)	GLC and HPLC	0
Benzo[g,h,i]perylene (ppm)	GLC and HPLC	0
Chrysene (ppm)	GLC and HPLC	0
Benzo[a]fluoranthene + Benzo[k]fluoranthene (ppm)	GLC and HPLC	0
Benzo[b]fluoranthene (ppm)	GLC and HPLC	0
Optical anisotropy (% by volume)	ASTM D 4616	0

[0096] The above-mentioned pitch showed no trace of benzo[a]pyrene or of the other aromatic compounds given in Tables 1A and 4B, determined by gas-liquid chromatography (GLC) and liquid-liquid chromatography (HPLC), and also had zero optical anisotropy.

[0097] Naturally, in order to produce pitches with specific QI, TI and coke characteristics, an expert in the art will be able to use, in the method of the invention, residues of the distillation of tar and/or petroleum with QI, TI and coke characteristics and contents of polycyclic aromatic compounds other than those mentioned in the foregoing examples.

[0098] These pitches will in any case always be produced substantially free of benzo[a]pyrene and will have optical anisotropy of less than 1%.

#### EXAMPLE 5

[0099] 100 parts by weight of the pitch produced in accordance with the method of Example 1, and having the characteristics given in Table 1B were mixed with 25.5 parts by weight of an aromatic oil completely free of benzo[a]pyrene and having, in accordance with the ASTM-D86 method, an initial distillation point of 245°C and a final distillation point of 300°C.

[0100] A pitch having the following characteristics given in Table 5A was thus produced:

TABLE 5A

Parameters	Analytical method	Value
Mettler softening temperature (°C)	ASTM D 3104	107.0
Insoluble in quinoline Q.I. (% by weight)	ISO 6791	19.4
Insoluble in toluene, T.I. (% by weight)	ISO 6376	53.5
Benzo[a]anthracene (ppm)	GLC + HPLC	0
Benzo[e]pyrene (ppm)	GLC + HPLC	0
Benzo[a]pyrene (ppm)	GLC + HPLC	0
Indeno[1,2,3-c,d]pyrene (ppm)	GLC + HPLC	0
Dibenzo[a,h]anthracene (ppm)	GLC + HPLC	0

TABLE 5A (continued)

Parameters	Analytical method	Value
Benzo[g,h,i]perylene (ppm)	GLC + HPLC	0
Chrysene (ppm)	GLC + HPLC	0
Benzo[a]fluoranthene + Benzo[k]fluoranthene (ppm)	GLC + HPLC	0
Benzo[b]fluoranthene (ppm)	GLC + HPLC	0
Optical anisotropy(% by volume)	ASTM D 4616	0

[0101] This pitch can advantageously be used as a binding agent for the production of electrodes, for example, for the steel industry, the aluminium industry, etc.

#### EXAMPLE 6

[0102] 100 parts by weight of the pitch produced in accordance with the method of Example 2 and having the characteristics given in Table 2B were mixed with 30 parts by weight of an aromatic oil completely free of benzo[a]pyrene and having, in accordance with the ASTM-D86 method, an initial distillation point of 245°C and a final distillation point of 300°C.

[0103] A pitch which had the following characteristics given in Table 6A was thus produced:

TABLE 6A

Parameters	Analytical method	Value
Mettler softening temperature (°C)	ASTM D 3104	92.0
Insoluble in quinoline Q.I. (% by weight)	ISO 6791	0.8
Insoluble in toluene T.I. (% by weight)	ISO 6376	13.4
Alcan coke yield (% by weight)	ASTM D 4715	55.2
Benzo[a]anthracene (ppm)	GLC + HPLC	0
Benzo[e]pyrene (ppm)	GLC + HPLC	0
Benzo[a]pyrene (ppm)	GLC + HPLC	0
Indeno[1,2,3-c,d]pyrene (ppm)	GLC + HPLC	0
Dibenzo[a,h]anthracene (ppm)	GLC + HPLC	0
Benzo[g,h,i]perylene (ppm)	GLC + HPLC	0
Chrysene (ppm)	GLC + HPLC	0
Benzo[a]fluoranthene + Benzo[k]fluoranthene (ppm)	GLC + HPLC	0
Benzo[b]fluoranthene (ppm)	GLC + HPLC	0
Optical anisotropy (% by volume)	ASTM D 4616	0

[0104] This pitch can advantageously be used as an impregnation agent for electrodes and also as an impregnation and/or binding agent for aluminium anodes and for refractory materials.

[0105] Naturally, an expert in the art will be able to mix pitches produced in accordance with the method of the invention with different viscosity-modifying agents free of benzo[a]pyrene, having different characteristics from those of the oils mentioned in Examples 5 and 6, and/or will be able to use different mixing ratios so as to produce pitches more specifically suitable for individual uses/users' various requirements for characteristics/workability.

#### Claims

1. Tar and/or oil pitch with a low content of polycyclic aromatic substances, characterized in that it has a benzo[a]pyrene content less than or equal to 5 ppm, and in that it has optical anisotropy of less than 1%.

2. Pitch according to Claim 1, characterized in that it is free of benzo[a]pyrene.
3. Pitch according to Claim 1 or Claim 2, characterized in that it has a content of less than 50 ppm of each of the following polycyclic aromatic compounds: benzo[a]anthracene, chrysene, benzo[a]fluoranthene, benzo[k]fluoranthene, benzo[b]fluoranthene, benzo[e]pyrene, indeno[1,2,3-c,d]pyrene, dibenzo[a,h]anthracene and benzo[g,h,i]perylene.
4. Pitch according to Claim 3, characterized in that the content of at least one of the said polycyclic aromatic compounds is less than 5 ppm.
5. Pitch according to Claim 3, characterized in that it is free of all of the said polycyclic aromatic compounds.
6. Pitch according to any one of the preceding claims, characterized in that it has zero optical anisotropy.
7. A method of preparing a tar and/or oil pitch according to any one of the preceding claims, comprising the steps of:
  - performing a first distillation of tar and/or petroleum so as to produce a residue with a low softening point;
  - supplying the residue or a mixture of the residue with tar and/or petroleum into an evaporator having a heat-exchange area:volume ratio of between  $1 \text{ m}^2/\text{m}^3$  and  $200 \text{ m}^2/\text{m}^3$ , the residue or the mixture being kept in a state of continuous mixing;
  - distilling the residue or the mixture with continuous mixing, in the evaporator, at a pressure less than or equal to 10 mbars and at a temperature of between  $250^\circ\text{C}$  and  $360^\circ\text{C}$ , for a period of at least 20 minutes;
  - discharging the pitch from the evaporator and, at the same time, recovering a distillate.
8. A method according to Claim 7, in which the distillation of the residue or the mixture comprises the steps of:
  - providing an evaporator (R) having a heat-exchange area:volume of between  $1 \text{ m}^2/\text{m}^3$  and  $200 \text{ m}^2/\text{m}^3$  and comprising a cylindrical body (1) provided with a jacket (2) for heating its internal wall (13), at least one inlet opening (3) for the residue or the mixture, at least one outlet opening (4) for the pitch, at least one distillate-recovery opening (5) connected to a system for applying a reduced pressure to the interior of the cylindrical body (1), and a rotary shaft (6) which can be heated and is supported for rotating in the cylindrical body (1), and along the axis of which radial mixing elements (9) which may also be capable of being heated, are disposed;
  - supplying the residue or the mixture into the evaporator in which the internal wall (13), the rotary shaft (6), and possibly the mixing elements (9) are kept at a temperature of  $250\text{-}360^\circ\text{C}$ , the rotary shaft (6) is rotated at a speed of 1-150 revolutions/minute, and the pressure is less than or equal to 10 mbars;
  - mixing the residue or the mixture for a period of at least 20 minutes by means of the mixing elements (9) in a relationship permitting thermal exchange with the internal wall (13) of the evaporator, the rotary shaft (6) and, possibly, the mixing elements (9),
  - discharging the pitch from the evaporator and, at the same time, recovering a distillate.
9. A method according to Claim 8, in which the radial mixing elements (9) comprise disc sectors (11) to which mixing bars (12) are fixed.
10. A method according to Claim 8 or Claim 9, in which the evaporator (R) further comprises opposed mixing elements (10) fixed radially to the internal wall (13) of the cylindrical body (1) and interposed between the mixing elements (9).
11. A method according to Claim 10, in which the fixed opposed elements (10) are substantially hook-shaped with at least one portion (20) skimming the disc sectors (11) and at least one portion (21) skimming the peripheral surface of the shaft (6).
12. A method according to any one of Claims 7 to 11, in which the evaporator has a heat-exchange area:volume ratio of between  $5 \text{ m}^2/\text{m}^3$  and  $60 \text{ m}^2/\text{m}^3$ .
13. A method according to any one of Claims 7 to 12, in which the time for which of the residue or mixture is distilled in the evaporator is between 20 minutes and 10 hours.

**14.** A composition comprising at least one pitch according to any one of Claims 1 to 6 and at least one viscosity-modifying agent substantially free of benzo[a]pyrene.

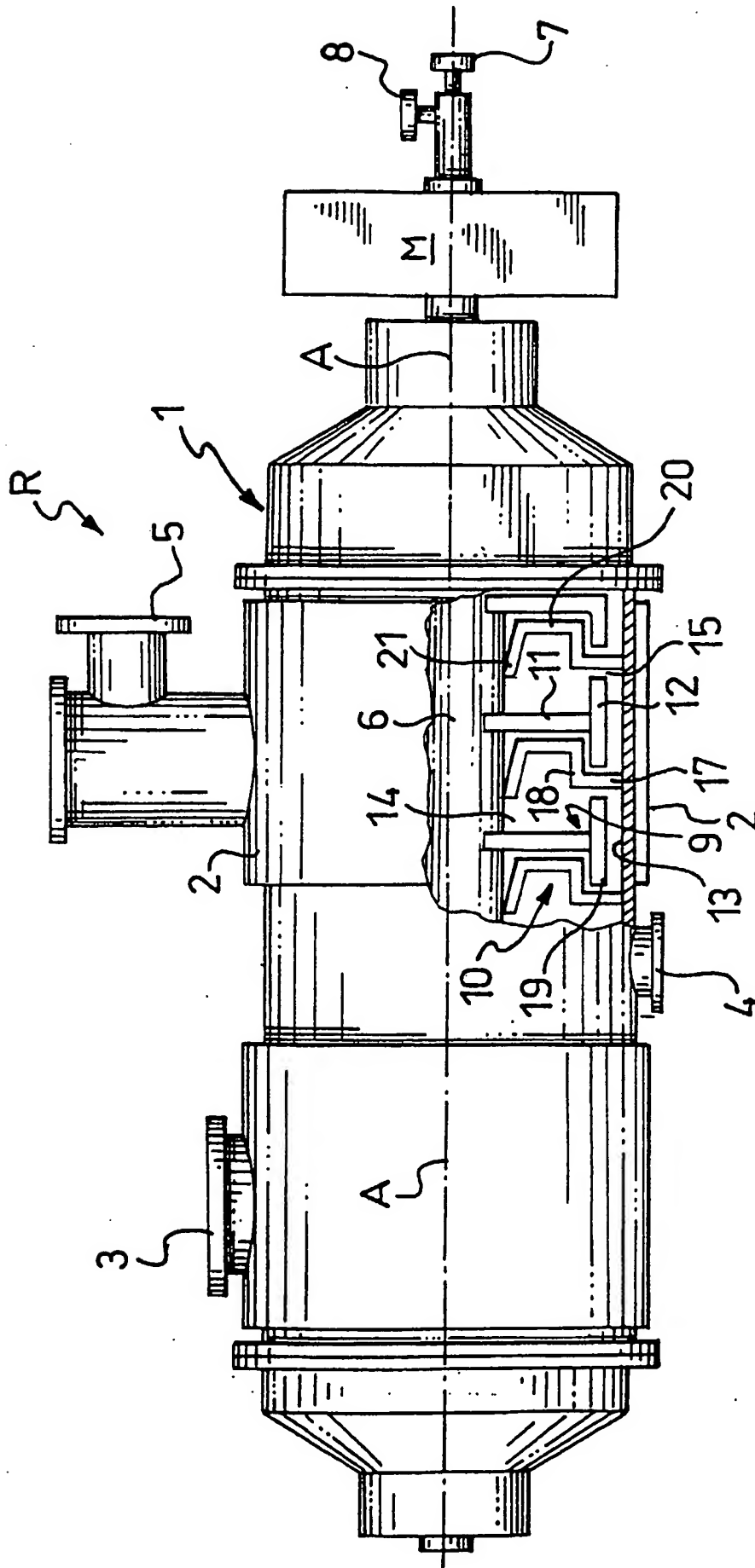
**15.** Use of a composition according to Claim 14 as a binding agent.

**16.** Use of a composition according to Claim 14 as an impregnating agent.

**17.** Use of a composition according to Claim 14 in the production of paints.

**18.** Use of a composition according to Claim 14 in the production of pitch coke.

**19.** Use of a composition according to Claim 14 in the production of rechargeable batteries.





European Patent  
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# EUROPEAN SEARCH REPORT

Application Number  
EP 98 83 0298

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
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The present search report has been drawn up for all claims			
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THE HAGUE	20 October 1998	Rotsaert, L	
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone  Y : particularly relevant if combined with another document of the same category  A : technological background  O : non-written disclosure  P : intermediate document</p> <p>T : theory or principle underlying the invention  E : earlier patent document, but published on, or after the filing date  D : document cited in the application  L : document cited for other reasons  .....  &amp; : member of the same patent family, corresponding document</p>			

**ANNEX TO THE EUROPEAN SEARCH REPORT  
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EP 98 83 0298

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on  
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